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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002950614 for a patent by JENS BIRGER NILSSON as filed on 07 August 2002.

WITNESS my hand this
Thirteenth day of August 2003

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AUSTRALIA
Patents Act 1990

Provisional Specification

Invention Title: A FLAME RETARDANT

The invention is described in the following statement:

A FLAME RETARDANT

This invention relates to the development of a chemical composition having fire retardant properties for application to fire to assist in the control or extinguishing of fire, or to assist in prevention of fire ignition or re-ignition.

The development of this invention originates from studies over a period of about 15 years into exothermic and endothermic reactions involving organic food-acids and their salts, and to produce an effective fire retardant having the endothermic capacity to absorb large amounts of heat energy, as well as the criteria of being cost-effective, environmentally friendly, and non-toxic.

Fire has been traditionally combated by the use of water. The efficiency of water as a fire combating agent has been improved over time by the addition of various materials, some as physical particle suspension systems such as liquid clay suspensions and emulsions, and others as water-soluble chemical solutions or mixtures. Other additives are also commonly employed such as; surfactants to aid wetting, dispersion, or penetration; foaming agents such as low boiling point chemicals; or methods such as the incorporation of compressed gases to produce foams. Many of these materials and methods suffer inherent disadvantages such as toxicity, corrosive properties, environmentally detrimental, or are expensive to produce. The Phosphates of Sodium, Potassium or Ammonium, for example, have relatively low thermal decomposition temperatures and can produce toxic gases, as well as leaving a troublesome sticky residue or powder, and are also now regarded as being potentially detrimental to the environment in that they are capable of promoting blue-green algae in waterways. The Halons have particular disadvantages in respect of the environment as many can produce toxic gases and incur damage to the earth's ozone layer to the extent that Halons are being discontinued from manufacture and legislation has been initiated to prohibit future usage. The potential health risks to all organic biological life including genetic risk of many chemicals currently used in todays society is of serious concern and fire retardants are of focus in this regard. Current trends are towards less environmental impact and include compressed air-foam systems (CAFS), and highly-alkaline salts such as Potassium Acetate, tri-Potassium Citrate, or Potassium Lactate which rely on the saponification of fats as a consequence of the high alkalinity at pH values of about 8 to 11, and which cannot be regarded as environment-friendly at these levels of alkalinity, and are constricted to use against burning oil, grease, or fats.

The present invention overcomes many of the disadvantages of previous fire retardants. The fire retardant of this invention can be demonstrated to be an effective fire retardant, is able to absorb large quantities of heat energy, can be applied as a surface protection to materials to prevent ignition, re-ignition, or the spread of fire, and may be considered cost-effective as it is relatively inexpensive to produce, is environmentally friendly as the major component(s) will undergo bio-degradation, is near-neutral in terms of pH value when made in accordance to this invention, and is an ionic water-soluble solution of non-toxic ingredients which will not cause any adverse skin effects and does not contain any toxic or carcinogenic substances and it is capable of being classified "non-hazardous" according to Worksafe Australia criteria.

The retardant of this invention offers the potential of use as a cost effective, non-toxic environment friendly, fire or flame combating agent in applications such as bushfire control, hose or pipe distribution systems such as sprinkler systems wherein the near-neutral pH reduces or eliminates corrosion effects and the low freezing point temperature of the retardant of below 20°C overcomes the problems of blocked or fractured supply lines. Other applications in which fire hazard can be reduced include industrial processes employing heat treatment, welding and oxy-cutting, and drilling, particularly in mining operations. The retardant can be employed to advantage in storage of flammable products. Textiles can be effectively treated, particularly in conjunction with a suitable environment-friendly Surfactant enabling reduction of surface tension to allow full penetration coverage of the fibres, without affecting the colour or form.

The objects of this invention are to provide efficient methods of manufacture, utilising the highly exothermic reactions of organic food acids with inorganic bases thereby generating large amounts of heat energy, and in which the raw material ingredients are substantially of natural origin, resulting in the provision of non-toxic, bio-degradeable, water-soluble salts having fire or flame retardant properties exemplified by good endothermic characteristics.

This invention is characterised as an ionic fire retardant consisting of a di-alkali-metal Citrate salt in which the alkali-metal cation is selected from the Group 1A alkali-metals Lithium, Sodium, and Potassium, and having a resultant pH value in the range of 6.5 to 7.5, by the addition of one or more Group 1A alkali-metal basic salts or compounds selected from the cations Lithium, Sodium, and Potassium, and the anions Acetate, Bicarbonate, Carbonate, and Hydroxide.

The preferred Citrate salt is di-Potassium Citrate and the preferred basic salt is Potassium Acetate. The retardant salt or salt mixture may optionally include a small amount of tetra-potassium Pyro-Phosphate, which is generally considered to be the least potentially harmful of the Phosphate family, to improve performance stability and endothermic capacity at higher temperatures.

The retardant may optionally include additional neutralising or buffering compounds such as, for example, Sodium Bicarbonate and/or Potassium Carbonate.

The preferred retardant has a pH value in the range of 7.0 to 7.2 and a preferred Specific Gravity value in the range of 1.2 to 1.4, and a typical analysis (approximate values) of the retardant when made as indicated in Example 7 is: pH=7.15, SG=1.365.

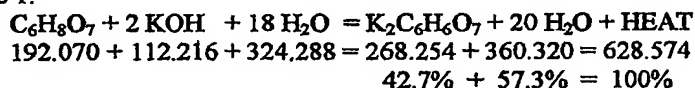|	
Citrate salt	20%
Acetate salt	28%
Phosphate salt	2%
Sodium Bicarbonate	3%
Water	47%

It should be noted that unless otherwise indicated, all percentages are percentages by weight referred to molecular weights, and all pH values and Specific Gravity values are in reference to measurements at 20°C. It should also be noted that the high salt concentrations will incur the "salt-effect" in respect of pH measurements. Solubility data should be consulted and taken into account for formulations in accordance with this invention.

The retardant may be manufactured from the raw material ingredient Citric Acid by controlled reaction with a basic salt or compound selected from the Group 1A alkali-metal cations of Lithium, Sodium, and Potassium, and the anions Acetate, Bicarbonate, Carbonate, and Hydroxide, to produce di-alkali-metal Citrate.

Citric Acid has a molecular weight of 192.070, a solubility of 622 gm/l (approx 3 gmw Citric Acid/55 gmw H_2O), and a pH in solution in water of between about 1.3 to about 2.0. It exhibits a temperature depression on solution (endothermic). Reaction of Citric Acid with basic substances generates considerable heat energy which is accompanied by frothing or foaming and care must be exercised to control the rate of reactant addition to keep the temperature down and avoid excessive foaming. In addition, the use of stainless steel mixing vessels and efficient mixing techniques will aid in heat dissipation and foam dispersion as well as increasing the efficiency of reaction.

The following Examples illustrate various aspects of the reactions involved, and of the preferred method of manufacturing.
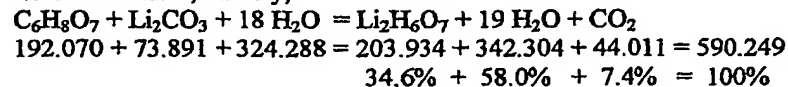
Example 1:-

$$C_6H_8O_7 + 2 KOH + 18 H_2O = K_2C_6H_6O_7 + 20 H_2O + HEAT$$
$$192.070 + 112.216 + 324.288 = 268.254 + 360.320 = 628.574$$
$$42.7\% + 57.3\% = 100\%$$

Solution of 1 gmw of Citric Acid in 18 gmw of water gave a pH of about 2.0. Controlled addition of 2 gmw of Potassium Hydroxide and keeping the temperature under 50°C results in the formation of mono-Potassium Citrate up to about pH 3.5 and then di-Potassium Citrate from about pH 3.5, up to about pH 5.2. A similar reaction comprising $9C_6H_8O_7 + 18KOH + 50 H_2O$ resulted in a pH of about 5.6.

Example 2:

In a similar manner to Example 1 but using Lithium Carbonate as the basic reactant with Citric Acid, namely,

$$C_6H_8O_7 + Li_2CO_3 + 18 H_2O = Li_2H_6O_7 + 19 H_2O + CO_2$$
$$192.070 + 73.891 + 324.288 = 203.934 + 342.304 + 44.011 = 590.249$$
$$34.6\% + 58.0\% + 7.4\% = 100\%$$

As the solubility of Lithium Carbonate is very low at 1.3 gm/l (1 gmw Li_2CO_3/313 gmw

H_2O), the Citric Acid is added to the water and then the Lithium Carbonate added as reactant. Less heat is generated in this reaction but the CO_2 evolution causes a considerable volume expansion as foam which must be mitigated with efficient mixing or stirring. As CO_2 is a "greenhouse" gas it should be collected for other use and
5   prevented from entering the atmosphere. The pH of the resultant di-Lithium Citrate is about 4.5.
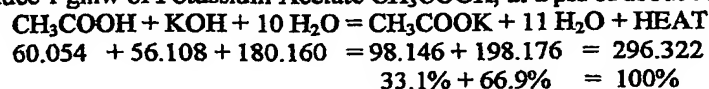
Example 3:-

In a similar manner,

$$2\ CH_3COOH + Li_2CO_3 + 8H_2O = 2\ CH_3COOLi + 9H_2O + CO_2$$
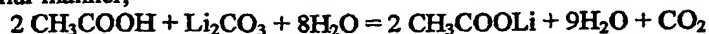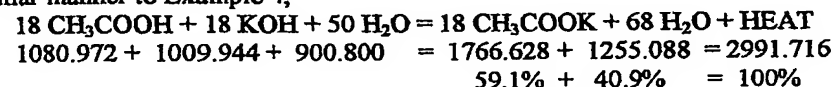
10   resulting at pH about 5.8.

Example 4:

To 10 gmw of H_2O is added 2 gmw of KOH slowly to control the heat of solution and Keep the temperature below about 50°C. Then 1 gmw of Acetic Acid is slowly added To produce 1 gmw of Potassium Acetate CH_3COOK, at a pH of about 9.5.

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$$CH_3COOH + KOH + 10\ H_2O = CH_3COOK + 11\ H_2O + HEAT$$
$$60.054\ \ + 56.108 + 180.160\ \ = 98.146 + 198.176\ \ = 296.322$$
$$33.1\% + 66.9\%\ \ = 100\%$$

Example 5:-

In a similar manner to Example 4,

20
$$18\ CH_3COOH + 18\ KOH + 50\ H_2O = 18\ CH_3COOK + 68\ H_2O + HEAT$$
$$1080.972 + \ 1009.944 + \ 900.800\ \ \ = 1766.628 + \ 1255.088\ = 2991.716$$
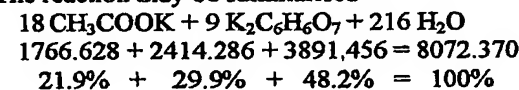$$59.1\%\ + \ 40.9\%\ \ \ = 100\%$$

This example reflects the minimum solubility requirement of KOH

Example 6:-

25   Solid CH_3COOK is dissolved in water which results in an alkaline solution having a pH of from about 8.7, up to about 11.1 at the limit of solubility which is 2530 gm/l or 25 CH_3COOK/55 H_2O. 18 CH_3COOK is added to 68 H_2O and dissolved . 18 KOH dissolved in 130 H_2O is then added followed by slow addition of solid Citric Acid. The reaction may be summarised –

30
$$18\ CH_3COOK + 9\ K_2C_6H_6O_7 + 216\ H_2O$$
$$1766.628 + 2414.286 + 3891.456 = 8072.370$$
$$21.9\%\ + \ 29.9\%\ + \ 48.2\%\ = \ 100\%$$

Example 7:

The ingredients are mixed in the following order:

35
Water (pH7.0)	33%
KOH (minimum 85% lye)	21%
CH_3COOH (minimum 96%)	10%
Citric Acid $C_6H_8O_7$ anhydrous	21%

At this stage the pH was measured at about 5.8, and SG = 1.310

40
K_2CO_3 anhydrous	8%
$K_4P_2O_7$ (minimum 99.5%)	2%
$NaHCO_3$ (minimum 99.5%	4%
Surfactant – Ampholak YCE Berol	1%

The pH is adjusted to the preferred value using additional amounts of KOH, K_2CO_3, or
45    $NaHCO_3$, or can also be adjusted by additional amounts of CH_3COOK, or Acetic or Citric acids as required.

The reactions of this Example may be summarised as:

$$180\ H_2O + 18\ KOH + 18\ CH_3COOH = 18\ CH_3COOK + 198\ H_2O$$
$$18\ CH_3COOK + 198\ H_2O + 18\ KOH + 9C_6H_8O_7 = 18\ CH_3COOK + 9\ K_2C_6H_6O_7 + 216\ H_2O$$
50
$$= 22\% + 30\% + 48\%$$
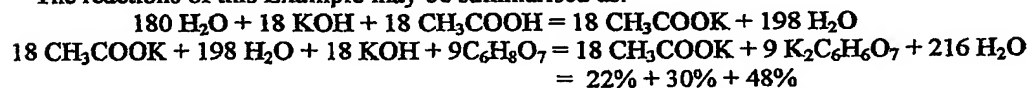
and on accounting for the additional ingredients will approximate to the typical analysis results described above.

The retardant when stored in an internal protected environment in a sealed container at room temperature has a shelf life in excess of 2 years. On exposure to external unprotected
55   Australian Autumn/Winter conditions it will biodegrade in less than 3 months.

Measurements of temperature, pH and Specific Gravity in respect of the foregoing Examples indicate that the pH of the retardant product can be readily adjusted or buffered to a value from about 4.5 to about 6.5, and advantage can be taken of this pH range to generate a near-neutral foam using the known "soda" or "soda-acid" principle using appropriate ratios of the retardant to alkali-metal salt or compound of which Sodium Bicarbonate or Potassium Carbonate are preferred. Experiments were conducted which showed that a considerable amount of foam can be generated and pH measurements of the resultant foam showed that the pH was near-neutral, within the range of 6.5 to 7.5.

The retardant of this invention is also ideal for combination with other expansion agents such as the protein-based agents or some of the Fluoroiodocarbons (FICS) which are said to be non-toxic and environmentally safe. Compressed air foam systems (CAFS) using the retardant of this invention in concentrate form, i.e. formulated for minimum water content which in practical terms is about 60-75% by weight, may be particularly advantageous as a common mix ratio is 0.2% concentrate by volume producing a foam (average expansion = 10) of 0.2% concentrate, 9.98% water and 98% air.

The foregoing description and Examples illustrate various aspects of the raw material ingredients, the retardant products, and several approaches to manufacture the retardant of this invention.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An ionic fire retardant consisting of a di-alkali-metal Citrate salt wherein the alkali-metal cation is selected from the Group 1A alkali-metals Lithium, Sodium, and Potassium, and having a resultant pH value in the range of 6.5 to 7.5, by the addition of one or more Group 1A alkali-metal salts or compounds selected from the cations Lithium, Sodium, and Potassium, and the anions Acetate, Bicarbonate, Carbonate, and Hydroxide.

2. The fire retardant of Claim 1 wherein the di-alkali-metal Citrate salt is di-Potassium Citrate.

3. The fire retardant of Claim 1 or 2 wherein the alkali-metal salt or compound is Potassium Acetate.

4. The fire retardant of any one of Claims 1 to 3 wherein the resultant pH value is in the range of 7.0 to 7.2.

5. The fire retardant of any one of claims 1 to 4 wherein the resultant Specific Gravity is in the range of 1.2 to 1.4.

6. The fire retardant of any one of Claims 1 to 5 with the addition of tetra-Potassium Pyro-Phosphate.

7. The fire retardant of any one of Claims 1 to 6 wherein the pH value is adjusted within the range of 4.5 to 6.5 for addition to a Group IA alkali- metal Bicarbonate or Carbonate to produce a fire retardant foam.

8. The fire retardant of any one or more of Claims 1 to 7 wherein an expansion agent, propellant, or compressed gas is added to produce a fire retardant foam.

9. A fire retardant substantially as herein described with reference to the Examples.

10. A method of producing a fire retardant as claimed in any one of Claims 1 to 9 wherein the raw material ingredients are combined in the order of Water, Alkali, Acetic Acid, and Citric Acid.

11. A method of producing a fire retardant as claimed in Claim 10 wherein the fire retardant is buffered or neutralised by addition of a Group IA alkali- metal Bicarbonate or Carbonate.

12. A method of producing a fire retardant wherein the di-alkali-metal Citrate salt, and the alkali-metal salt or compound, are each separately produced, and then combined.

13. A method of producing a fire retardant substantially as herein described with reference to the Examples.

Dated this 7th day of August, 2002.

Jens Birger Nilsson

ABSTRACT

An ionic fire retardant consisting of a di-alkali-metal Citrate salt such as di-Potassium Citrate having, on application to a fire or to prevent fire ignition or re-ignition, a pH value in the range of 6.5 to 7.5. The retardant is buffered or neutralised by the addition of one or more basic alkali-metal salts or compounds selected from the anion group consisting of Acetate, Carbonate, Bicarbonate, and Hydroxide. The retardant preferably has a Specific Gravity value in the range of 1.2 to 1.4, and a preferred pH value in the range of 7.0 to 7.2. The retardant may be buffered to a pH value in the range of 4.0 to 6.5 to provide a "soda-acid" retardant foam. Methods of producing the retardant are described.

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